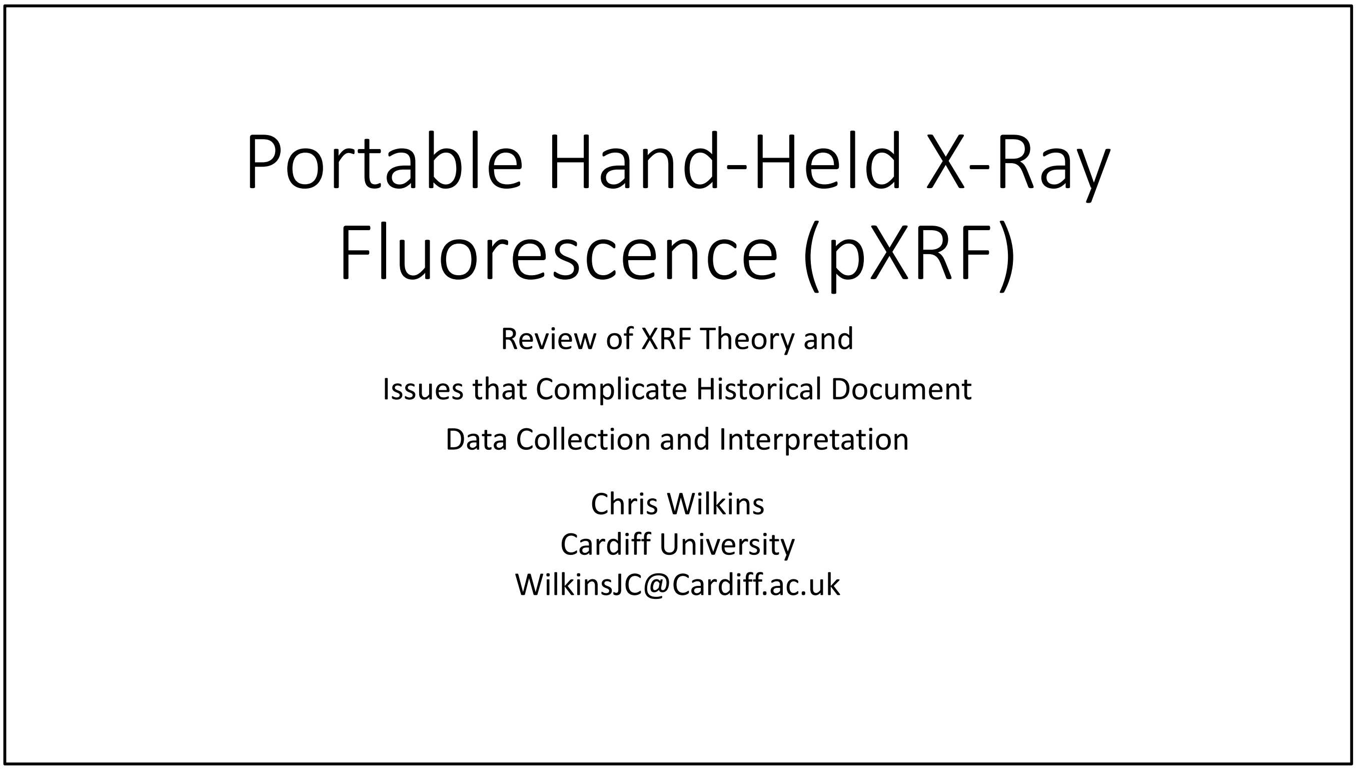


Portable Hand-Held X-Ray Fluorescence (pXRF)

Review of XRF Theory and
Issues that Complicate Historical Document
Data Collection and Interpretation

Chris Wilkins
Cardiff University
WilkinsJC@Cardiff.ac.uk

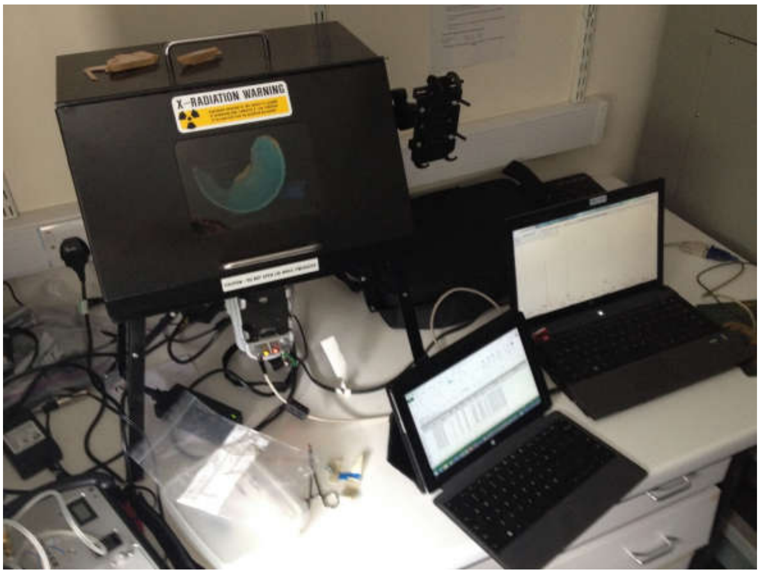
Presented at Icon Heritage Science Group’s ‘Historic document analysis using p-XRF: Pitfalls and Possibilities’, The National Archives UK, 11th September 2017.

Presentation notes reproduced for distribution via the Institute of Conservation’s website with the kind permission of the author.

Introduction – Benefits/Limitations – XRF Theory – Complication of Data Collection – Complication of Data Interpretation – Summary

pXRF

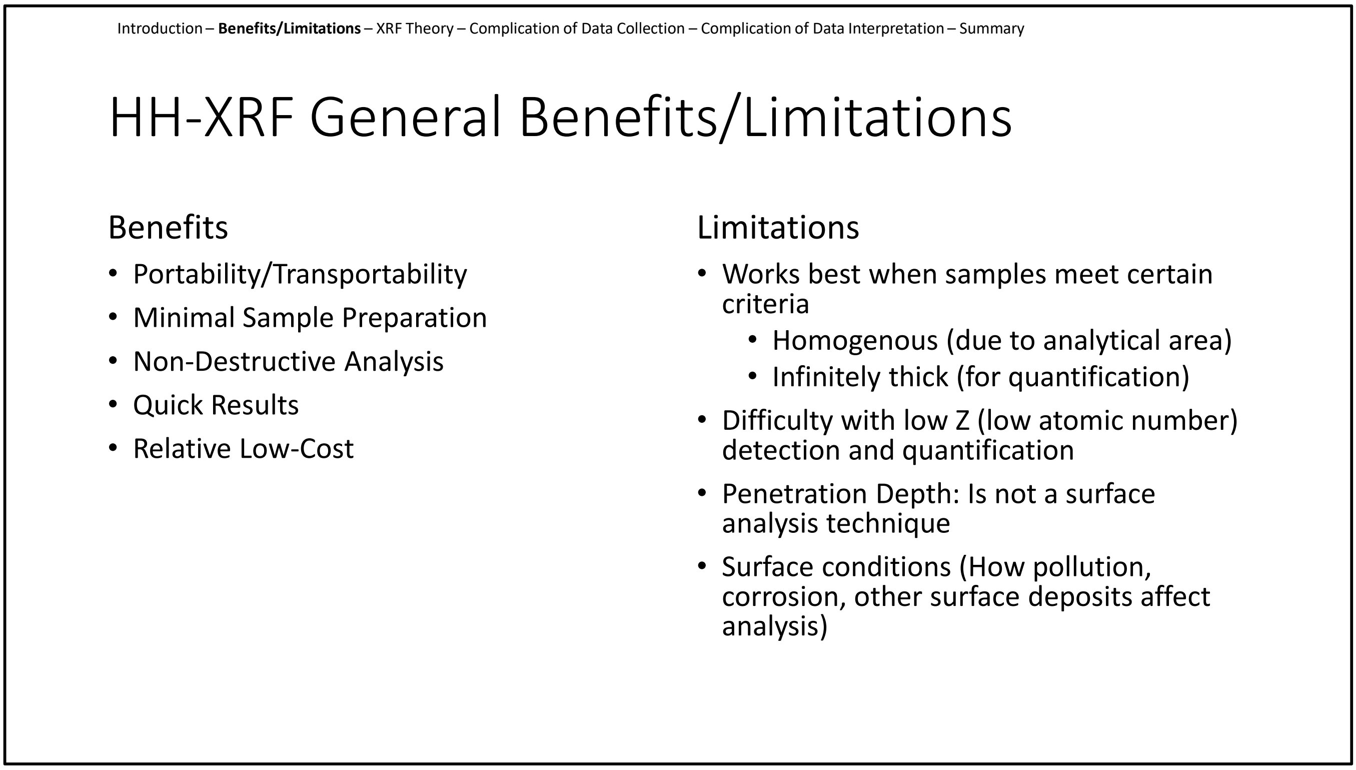
Bruker Tracer series using X-ray safety cabinet and laptop for data acquisition.



Introduction

What will be covered:

- General Benefits/Limitations of XRF
- XRF Theory
  - Bohrs Atomic Model
  - Generation of X-Rays and Bremsstrahlung Radiation
  - X-Ray Phenomena – Sample
  - X-Ray Phenomena – Detector
- Issues Complicating Historical Document pXRF Data Collection
  - Analyzer Setup
  - Sample Preparation
- Issues Complicating pXRF Data Interpretation
- Summary



Introduction – **Benefits/Limitations** – XRF Theory – Complication of Data Collection – Complication of Data Interpretation – Summary

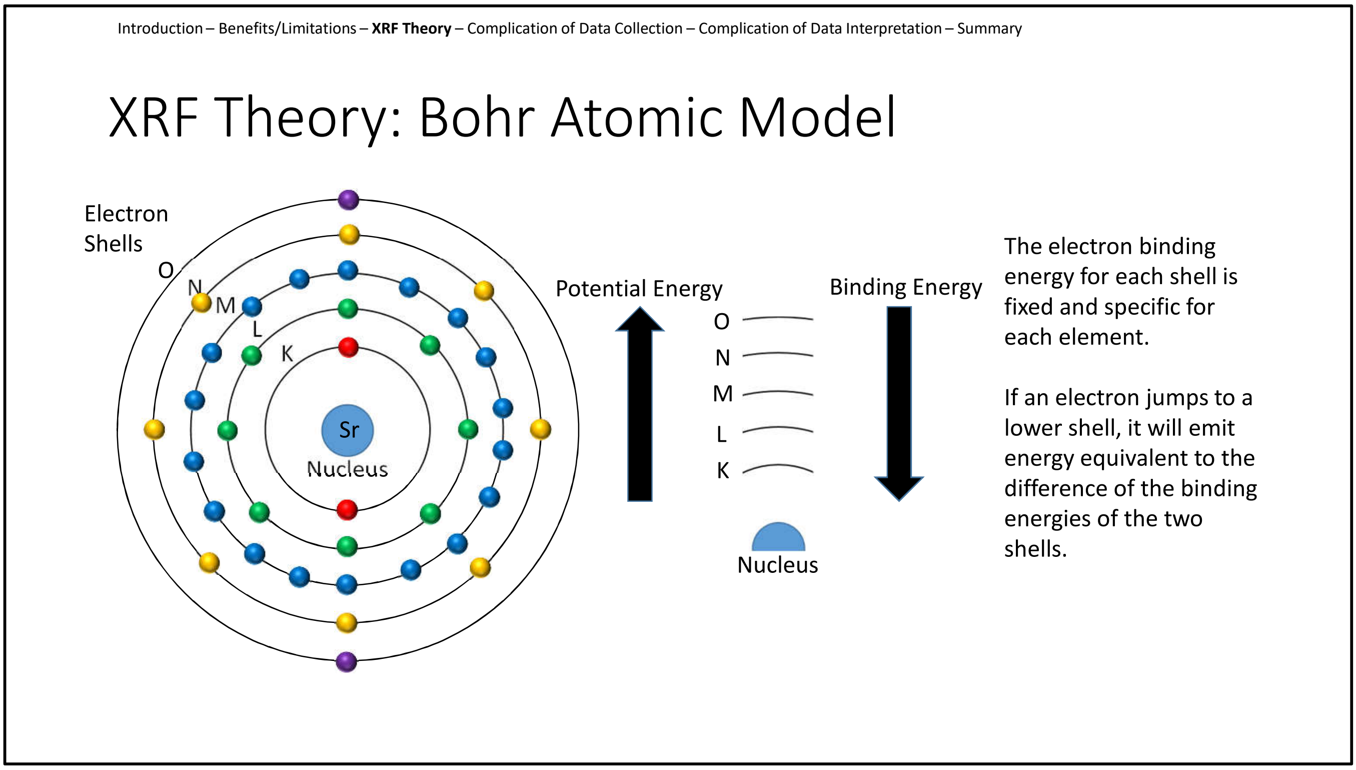
HH-XRF General Benefits/Limitations

Benefits

- Portability/Transportability
- Minimal Sample Preparation
- Non-Destructive Analysis
- Quick Results
- Relative Low-Cost

Limitations

- Works best when samples meet certain criteria
    - Homogenous (due to analytical area)
    - Infinitely thick (for quantification)
- Difficulty with low Z (low atomic number) detection and quantification
- Penetration Depth: Is not a surface analysis technique
- Surface conditions (How pollution, corrosion, other surface deposits affect analysis)



Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

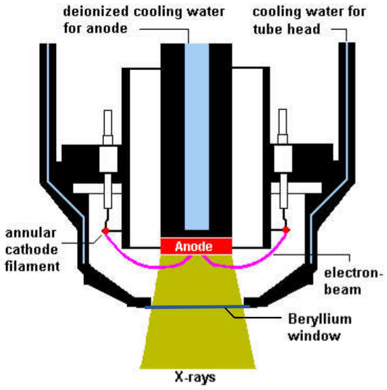
XRF Theory: Bohr Atomic Model

The electron binding energy for each shell is fixed and specific for each element.

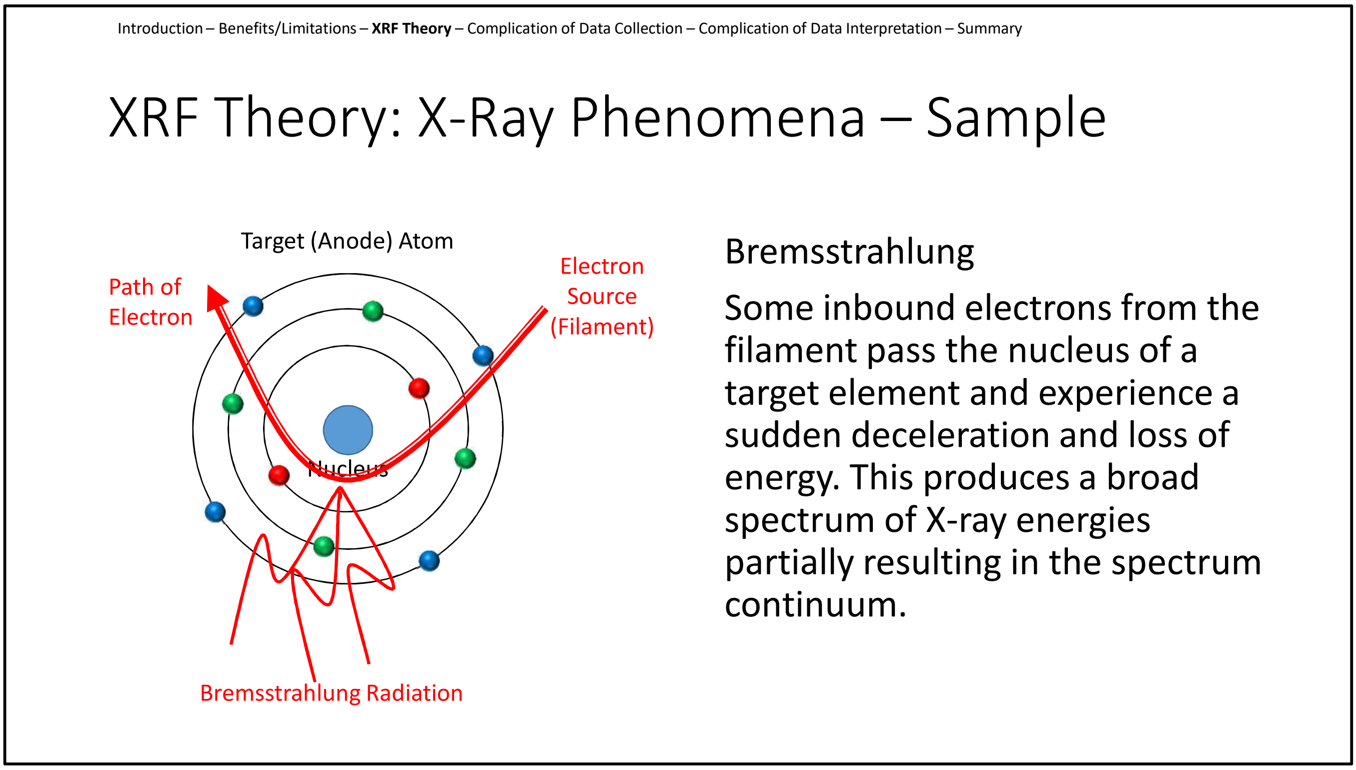
If an electron jumps to a lower shell, it will emit energy equivalent to the difference of the binding energies of the two shells.

XRF Theory: Generation of X-Rays

An electron beam striking the surface of the target (anode) produces 1-2% target X-ray photons and bremsstrahlung radiation from 0 keV up to the voltage selected for the analysis.



Schlotz, R. and Uhlig, S. 2006. *Introduction to X-Ray Fluorescence (XRF)*. Karlruhe, Germany: Bruker AXS GmgH. Figure 5



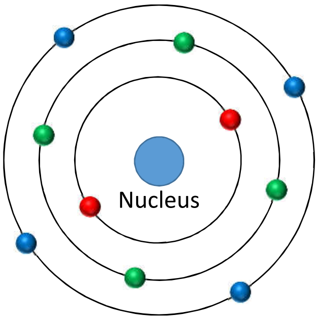
Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena – Sample

Bremsstrahlung

Some inbound electrons from the filament pass the nucleus of a target element and experience a sudden deceleration and loss of energy. This produces a broad spectrum of X-ray energies partially resulting in the spectrum continuum.

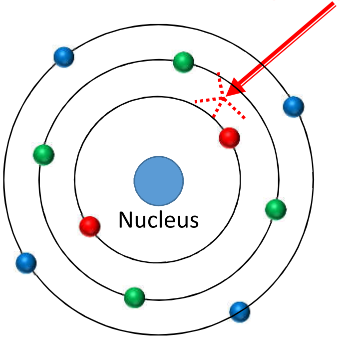
XRF Theory: X-Ray Phenomena - Sample



Five phenomena occur simultaneously when the target X-ray photons interact with an atom:

- Incident Beam Absorption
- Elastic Scattering (Rayleigh Scattering)
- Inelastic Scattering (Compton Scattering)
- Diffraction (Bragg Scattering)
- X-Ray Fluorescence (Characteristic Peaks)

XRF Theory: X-Ray Phenomena - Sample



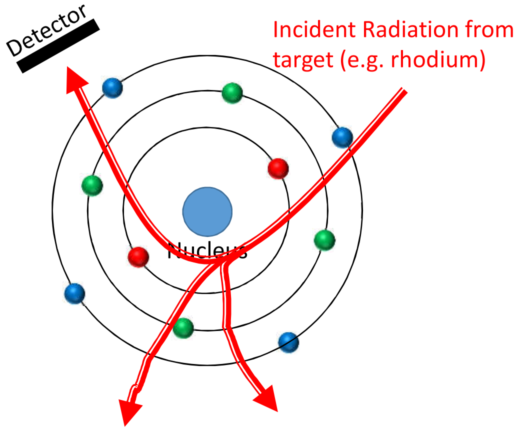
Incident Radiation from target (e.g. rhodium)

Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 1/5

- **Incident Beam Absorption**

The energy is absorbed into the atom but an electron is not ejected.

XRF Theory: X-Ray Phenomena - Sample

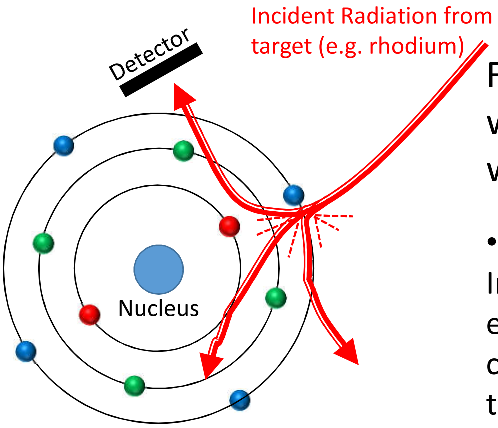


Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 2/5

- **Elastic Scattering (Rayleigh Scattering)**

Incident X-rays are scattered but do not lose energy. Some of these will be detected and will produce a peak on the spectrum representing the target material.

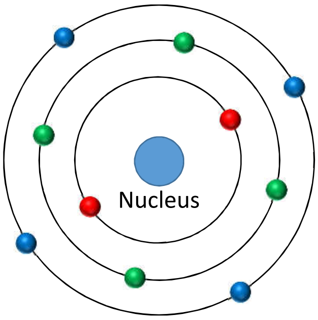
XRF Theory: X-Ray Phenomena - Sample



Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 3/5

- **Inelastic Scattering (Compton Scattering)** Incident radiation impacts an outer shell electron and loses some energy without causing an electron to be ejected. Some of these will be detected and will produce a broad peak (Compton peak) on the spectrum continuum slightly below the Rayleigh peak (representing the target material).

XRF Theory: X-Ray Phenomena - Sample

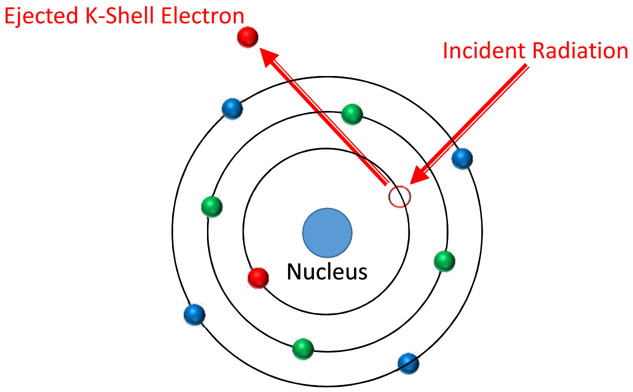


Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 4/5

- **Diffraction (Bragg Scattering)**

Incident radiation encounters different facets of crystalline material resulting in spurious peaks in the spectrum. Dependent on angle of incidence and will change as the angle is changed.

XRF Theory: X-Ray Phenomena - Sample

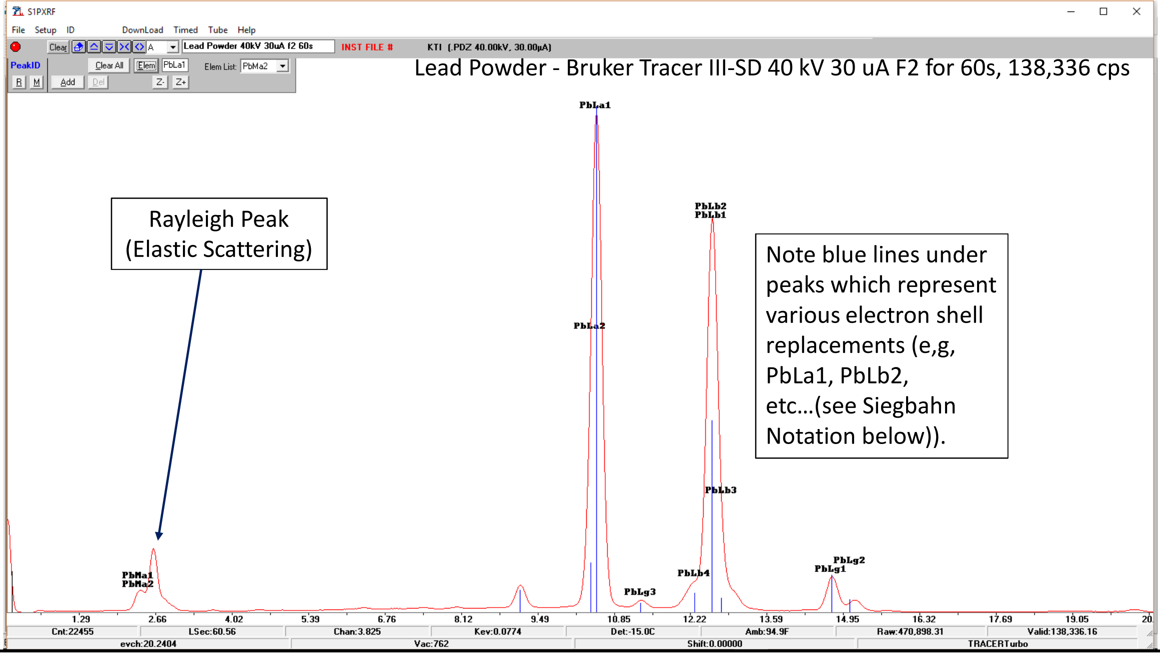


Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 5/5

- **X-Ray Fluorescence (Characteristic Peaks)**
Occurs when the incident radiation provides enough energy to force the ejection of an inner electron. Each element will have several characteristic peaks associated with it. The form in which the vacancy is filled determines the type of characteristic X-ray energy and characteristic peak produced (see Siegbahn Notation below).

Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Sample



Lead Powder 40kV 30uA f2 60s

KTI (.PDZ 40.00kV, 30.00µA)

Elem: PbLa1

Elem List: PbMa2

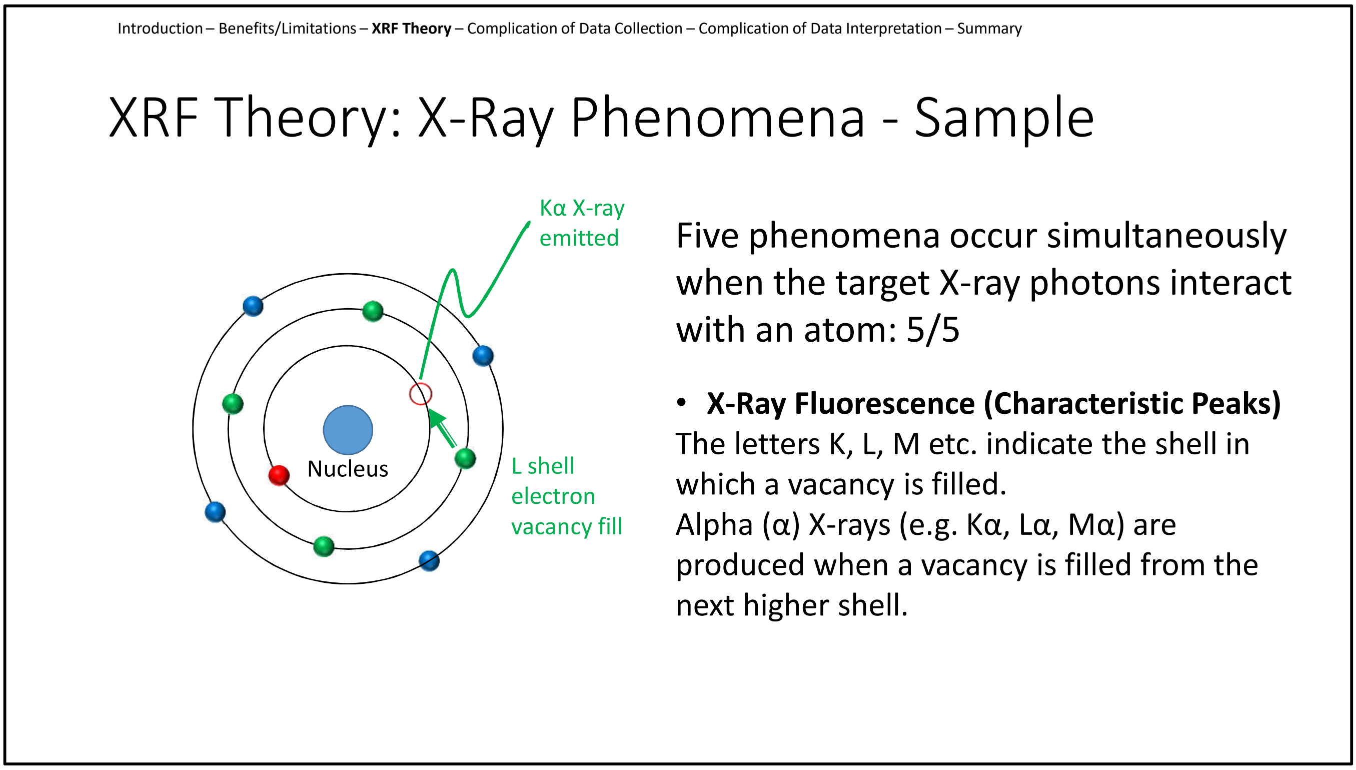
Lead Powder - Bruker Tracer III-SD 40 kV 30 uA F2 for 60s, 138,336 cps

Rayleigh Peak (Elastic Scattering)

Note blue lines under peaks which represent various electron shell replacements (e,g, PbLa1, PbLb2, etc…(see Siegbahn Notation below)).

Cnt:22455 LSec:60.56 Chan:3.825 Kev:0.0774 Det:-15.0C Amb:94.9F Raw:470,898.31 Valid:138,336.16

evch:20.2404 Vac:762 Shift:0.00000 TRACERTurbo



Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Sample

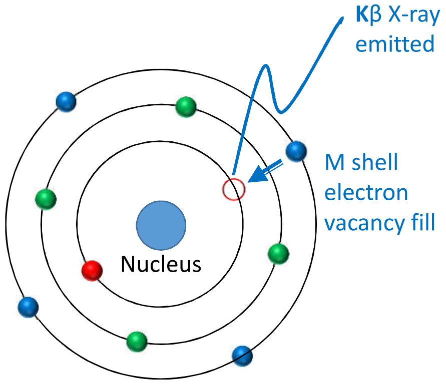
Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 5/5

- **X-Ray Fluorescence (Characteristic Peaks)**

The letters K, L, M etc. indicate the shell in which a vacancy is filled.

Alpha (α) X-rays (e.g. Kα, Lα, Mα) are produced when a vacancy is filled from the next higher shell.

XRF Theory: X-Ray Phenomena - Sample

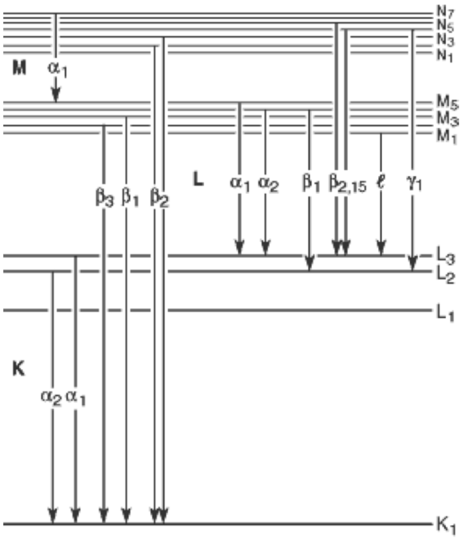


Five phenomena occur simultaneously when the target X-ray photons interact with an atom: 5/5

- **X-Ray Fluorescence (Characteristic Peaks)**

The letters K, L, M etc. indicate the shell in which a vacancy is filled.
Generally, beta (β) X-rays (e.g. Kβ, Lβ, Mβ) are produced when a vacancy is filled from two shells higher.

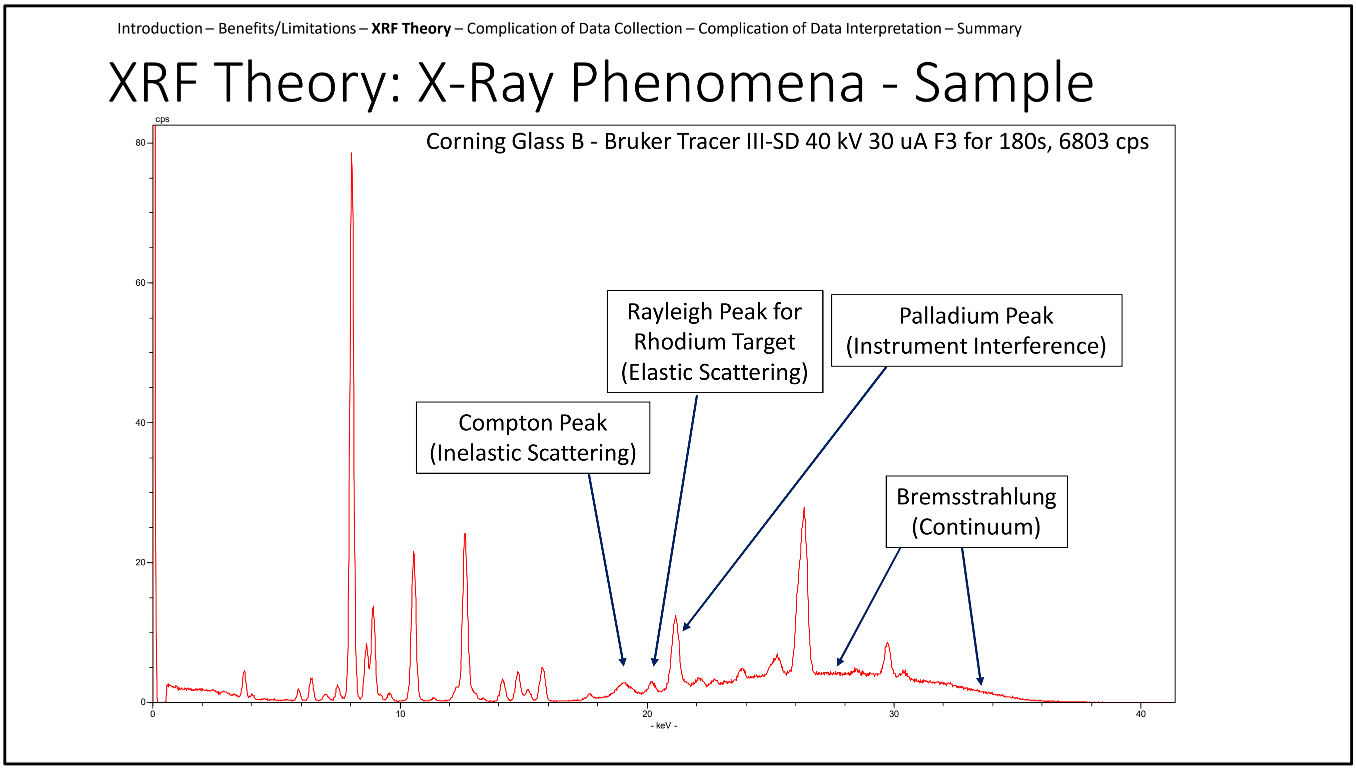
XRF Theory: X-Ray Phenomena - Sample



Electron Shell Movement Notation

This is known as Siegbahn Notation.

Examples: Kα_2 peak is produced when the K shell vacancy is filled by an L_2 subshell electron. Lβ_1 peak is produced when an L_2 subshell vacancy is filled by an M_4 subshell electron.
Siegbahn Notation Examples: "Copper Kα_2"; "Lead L Beta 1"



Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Sample

Corning Glass B - Bruker Tracer III-SD 40 kV 30 uA F3 for 180s, 6803 cps

Rayleigh Peak for Rhodium Target (Elastic Scattering)

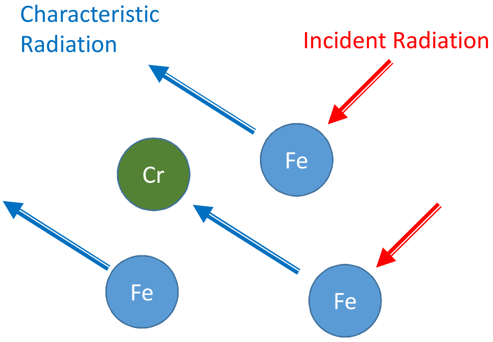
Palladium Peak (Instrument Interference)

Compton Peak (Inelastic Scattering)

Bremsstrahlung (Continuum)

Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Sample

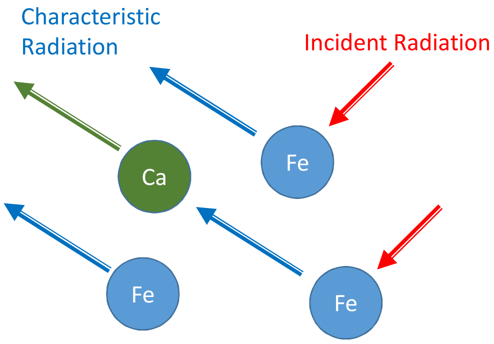


Matrix effects and other issues that will impact the analysis:

- **Absorption** } Mass Absorption Effects

Some of the characteristic X-rays may be absorbed by other atoms resulting in diminution of the detection of the element.

XRF Theory: X-Ray Phenomena - Sample



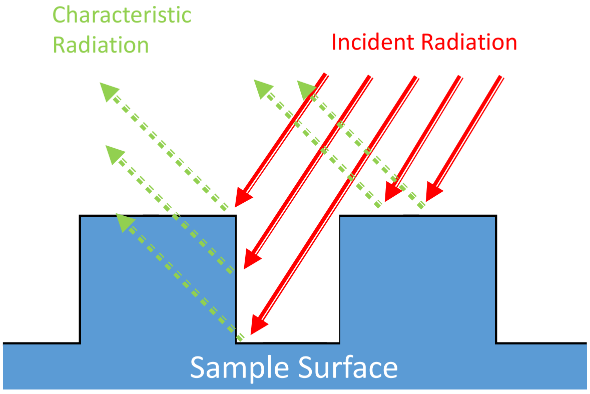
Matrix effects and other issues that will impact the analysis:

- Absorption
- **Secondary Excitation**

Mass Absorption Effects

Some of the characteristic X-rays may have enough energy to cause other elements to fluoresce resulting in enhancement of the secondary excited elements and diminution of the primary characteristic energy.

XRF Theory: X-Ray Phenomena - Sample

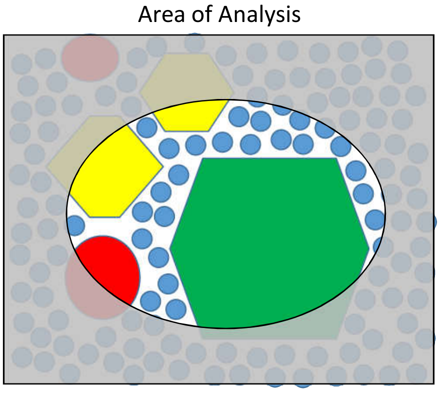


Matrix effects and other issues that will impact the analysis:

- Absorption
- Secondary Excitation
- **Surface Irregularities**

Convex, concave, or rough surfaces will produce inconsistent results. Increase in air column in cervices results in low Z shielding of characteristic energies. Signal may be further impacted by matrix effects when transmitted through elevated or thicker surface relief. Angle of incidence is inconsistent across a rough surface resulting in inefficient detection.

XRF Theory: X-Ray Phenomena - Sample



Matrix effects and other issues that will impact the analysis:

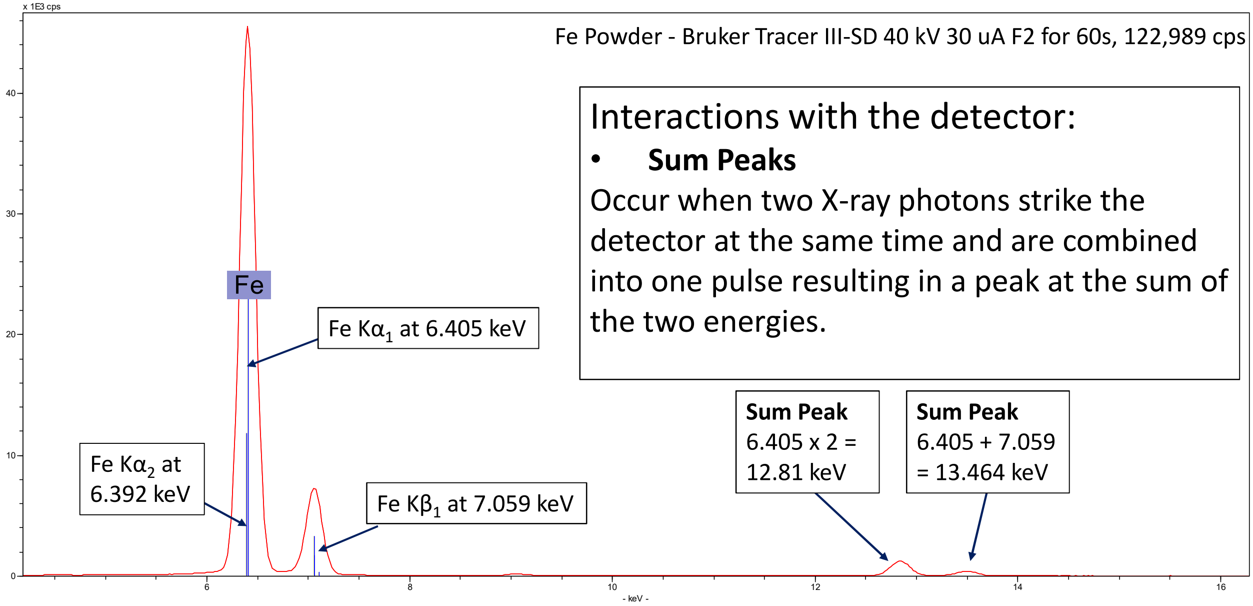
- Absorption
- Secondary Excitation
- Surface Irregularities
- **Particle Size**
- **Heterogeneity**

Mass Absorption Effects

Heterogeneity and particle size will impact element ratios and analytical accuracy. Some element ratios may be enhanced and others reduced due to inconsistent particle sizes.

Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Detector



Fe Powder - Bruker Tracer III-SD 40 kV 30 uA F2 for 60s, 122,989 cps

Interactions with the detector:

- **Sum Peaks**

Occur when two X-ray photons strike the detector at the same time and are combined into one pulse resulting in a peak at the sum of the two energies.

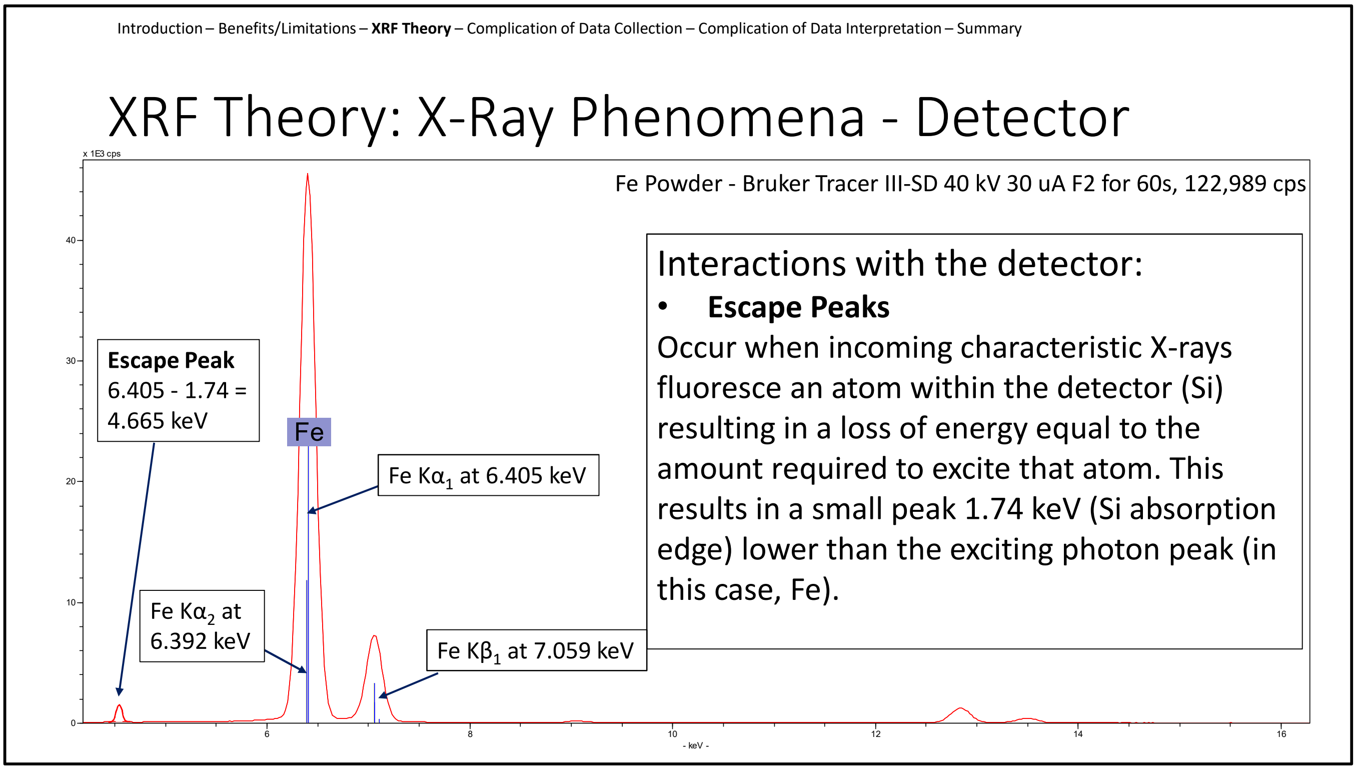
Fe Kα_1 at 6.405 keV

Fe Kα_2 at 6.392 keV

Fe Kβ_1 at 7.059 keV

Sum Peak
6.405 x 2 = 12.81 keV

Sum Peak
6.405 + 7.059 = 13.464 keV



Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena - Detector

Fe Powder - Bruker Tracer III-SD 40 kV 30 uA F2 for 60s, 122,989 cps

Interactions with the detector:

- **Escape Peaks**

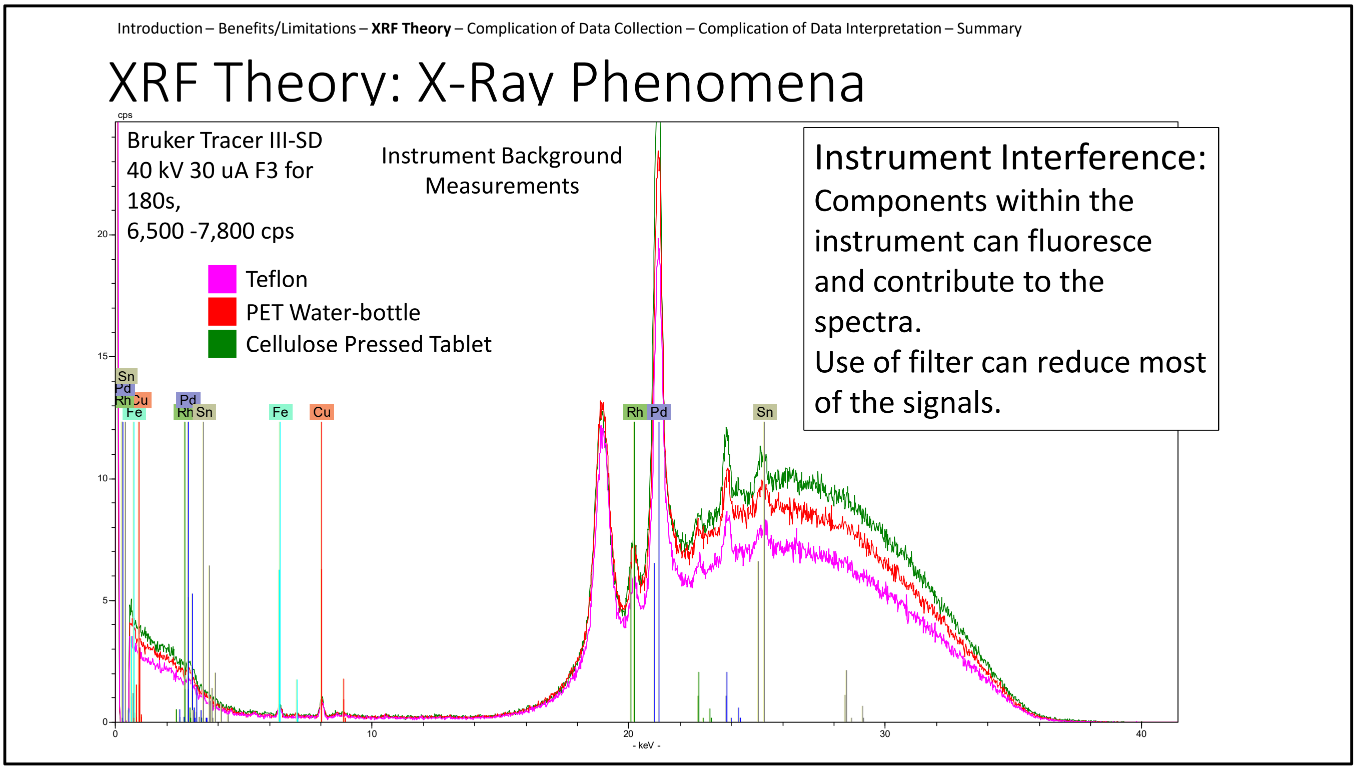
Occur when incoming characteristic X-rays fluoresce an atom within the detector (Si) resulting in a loss of energy equal to the amount required to excite that atom. This results in a small peak 1.74 keV (Si absorption edge) lower than the exciting photon peak (in this case, Fe).

Escape Peak
6.405 - 1.74 =
4.665 keV

Fe Kα_1 at 6.405 keV

Fe Kα_2 at 6.392 keV

Fe Kβ_1 at 7.059 keV



Introduction – Benefits/Limitations – **XRF Theory** – Complication of Data Collection – Complication of Data Interpretation – Summary

XRF Theory: X-Ray Phenomena

Bruker Tracer III-SD
40 kV 30 uA F3 for
180s,
6,500 -7,800 cps

Instrument Background Measurements

🟪 Teflon
🟥 PET Water-bottle
🟩 Cellulose Pressed Tablet

Instrument Interference:
Components within the instrument can fluoresce and contribute to the spectra.
Use of filter can reduce most of the signals.

Teflon has greatest density followed by cellulose and water bottle based on Compton peak height.

X-rays traveling from the source (the rhodium target) to the sample may fluoresce internal components of the HH-XRF unit resulting in trace peaks on the spectra (Kaiser and Wright 2008: 17-18). These contributions, as a group, are the *instrument signature* and are unique to each analyser unit.

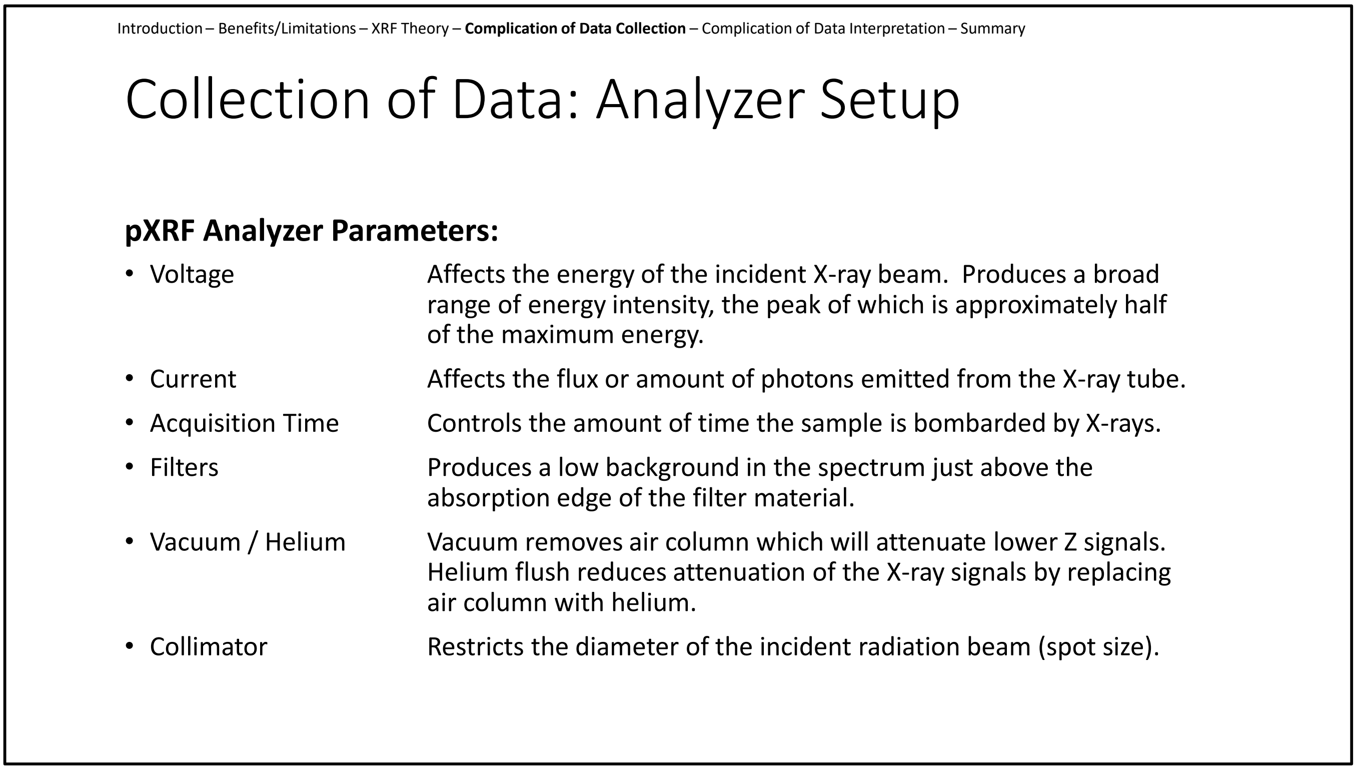
Rhodium (Rayleigh Scattering: X-ray Tube Target K and L lines)

Iron, Cobalt and Nickel (Detector Can)

Calcium (Window)

Aluminium, Copper, Palladium, and Zinc (Tube, Collimator, Unit Structure)

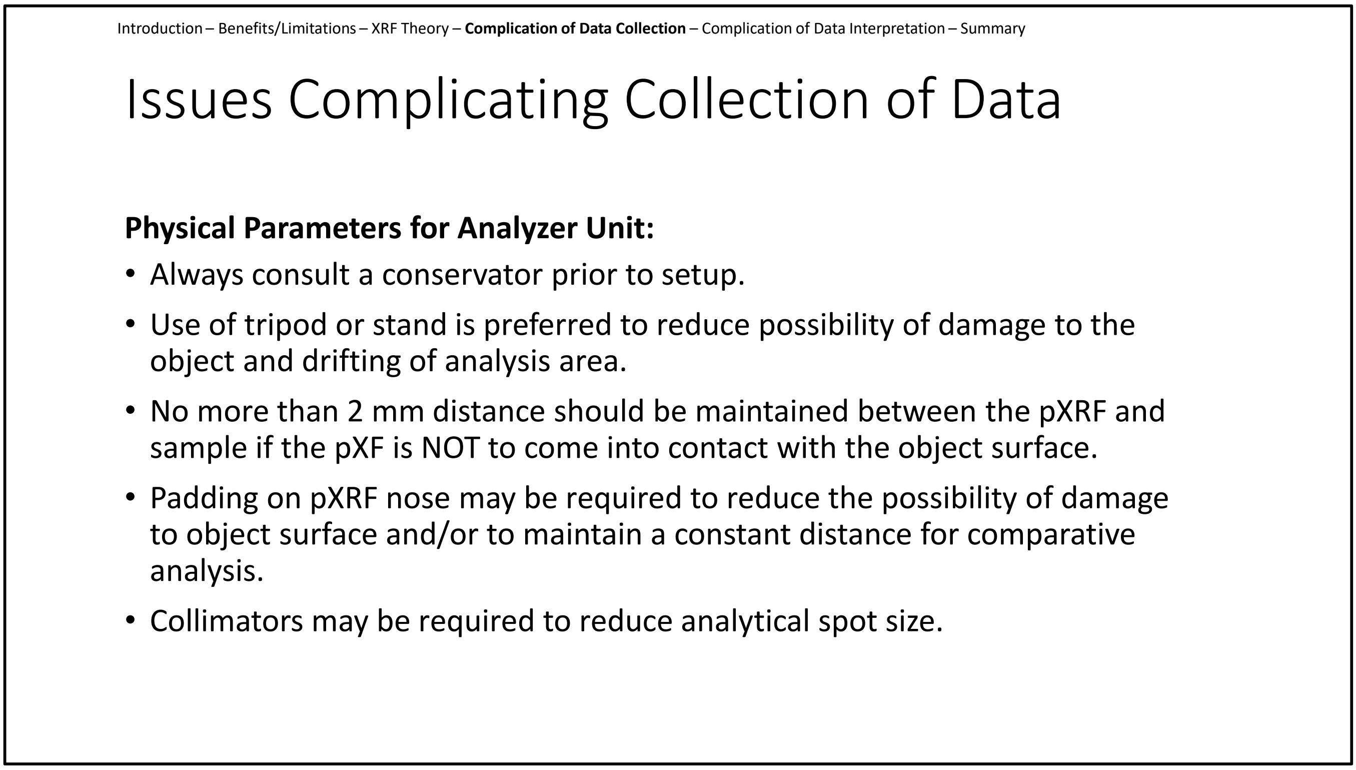
Bruker rep suggested Tin could be from solder.



Collection of Data: Analyzer Setup

pXRF Analyzer Parameters:

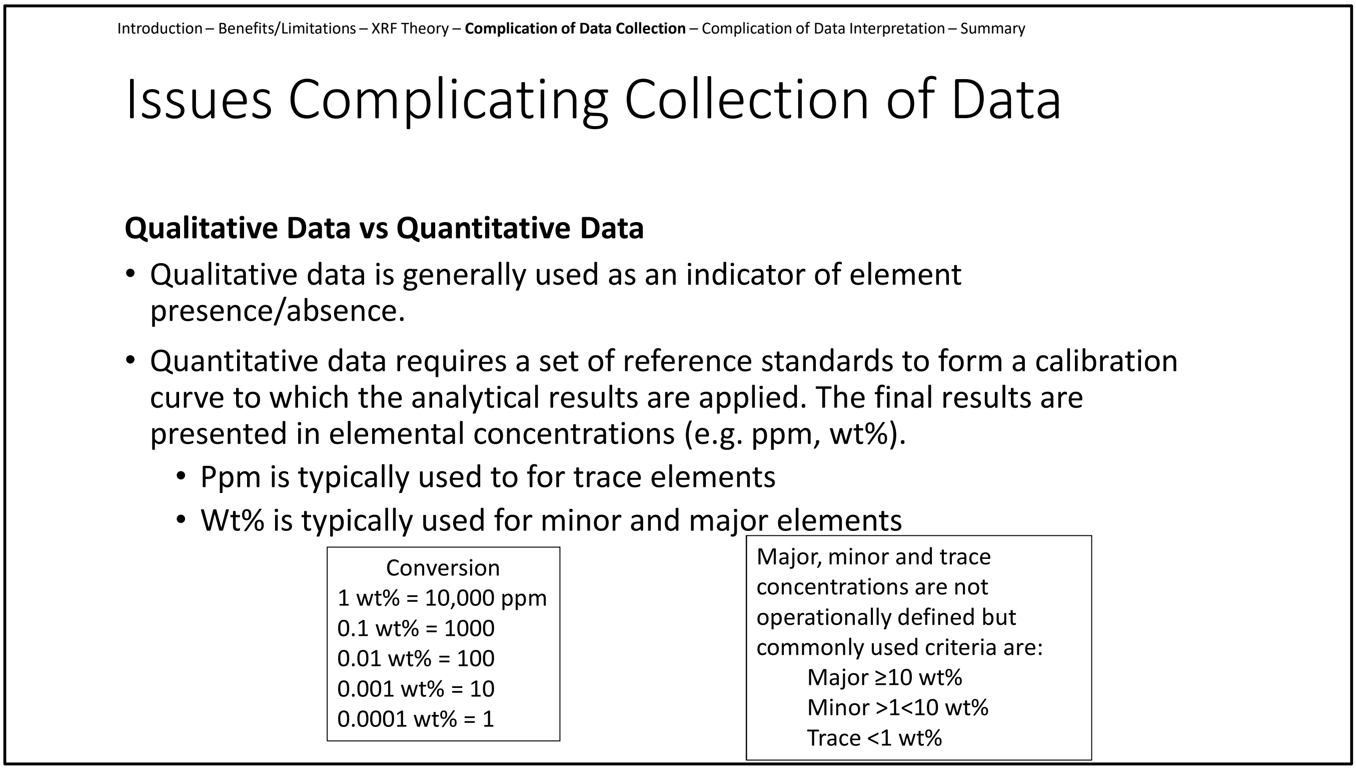
• Voltage	Affects the energy of the incident X-ray beam. Produces a broad range of energy intensity, the peak of which is approximately half of the maximum energy.
• Current	Affects the flux or amount of photons emitted from the X-ray tube.
• Acquisition Time	Controls the amount of time the sample is bombarded by X-rays.
• Filters	Produces a low background in the spectrum just above the absorption edge of the filter material.
• Vacuum / Helium	Vacuum removes air column which will attenuate lower Z signals. Helium flush reduces attenuation of the X-ray signals by replacing air column with helium.
• Collimator	Restricts the diameter of the incident radiation beam (spot size).



Issues Complicating Collection of Data

Physical Parameters for Analyzer Unit:

- Always consult a conservator prior to setup.
- Use of tripod or stand is preferred to reduce possibility of damage to the object and drifting of analysis area.
- No more than 2 mm distance should be maintained between the pXRF and sample if the pXF is NOT to come into contact with the object surface.
- Padding on pXRF nose may be required to reduce the possibility of damage to object surface and/or to maintain a constant distance for comparative analysis.
- Collimators may be required to reduce analytical spot size.



Issues Complicating Collection of Data

Qualitative Data vs Quantitative Data

- Qualitative data is generally used as an indicator of element presence/absence.
- Quantitative data requires a set of reference standards to form a calibration curve to which the analytical results are applied. The final results are presented in elemental concentrations (e.g. ppm, wt%).
  - Ppm is typically used to for trace elements
  - Wt% is typically used for minor and major elements

Conversion
1 wt% = 10,000 ppm
0.1 wt% = 1000
0.01 wt% = 100
0.001 wt% = 10
0.0001 wt% = 1

Major, minor and trace concentrations are not operationally defined but commonly used criteria are:

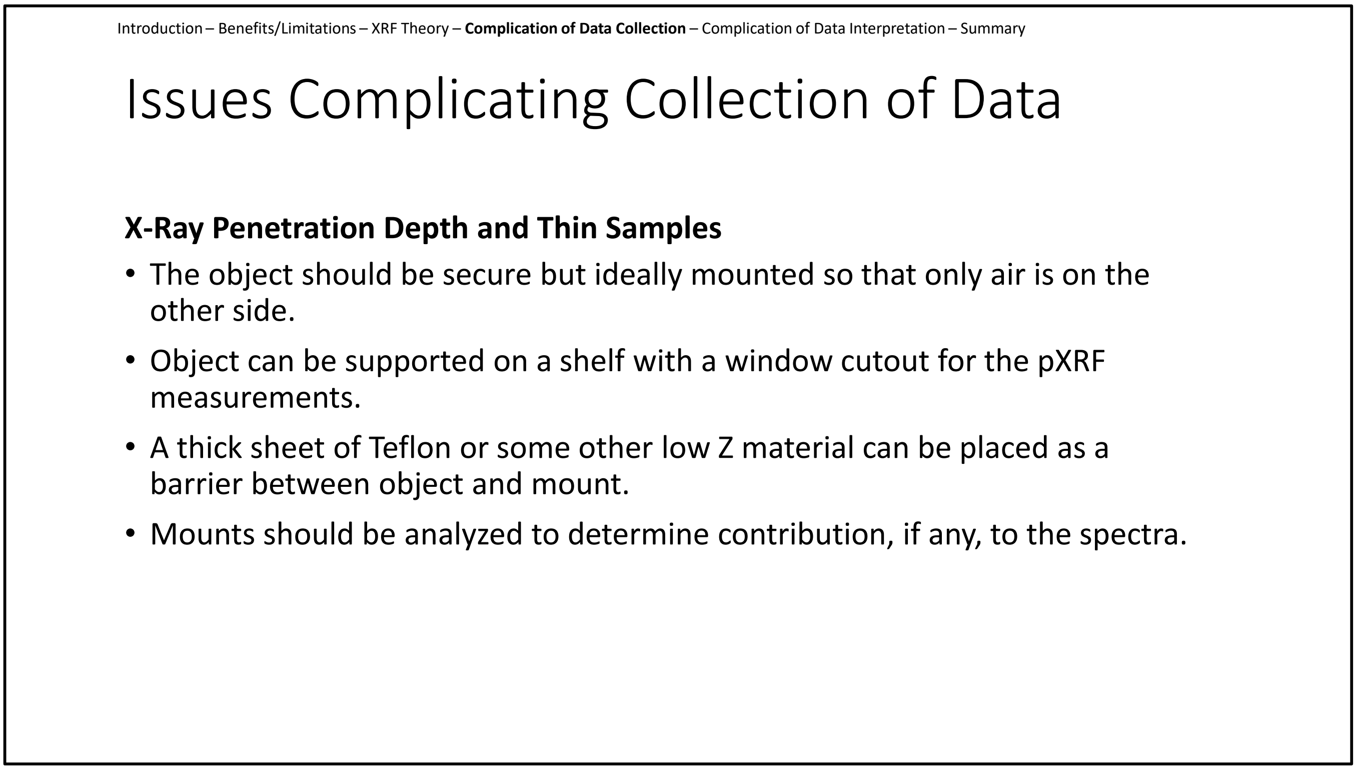
Major ≥10 wt%
Minor >1<10 wt%
Trace <1 wt%

Introduction – Benefits/Limitations – XRF Theory – **Complication of Data Collection** – Complication of Data Interpretation – Summary

Issues Complicating Collection of Data

Physical Parameters for Object:

- Objects should be secure to minimize potential damage.
- Weights or restrainment may be required for parchment and paper that may flex in the presence of minor air currents, changes in RH and temperature.
- Glassine can be used as a barrier for object surfaces susceptible to static electricity and flaking.
- Unnecessary handling of the object should be avoided.
- Positioning of object for analysis should conducted in a way that minimizes object stress.



Issues Complicating Collection of Data

X-Ray Penetration Depth and Thin Samples

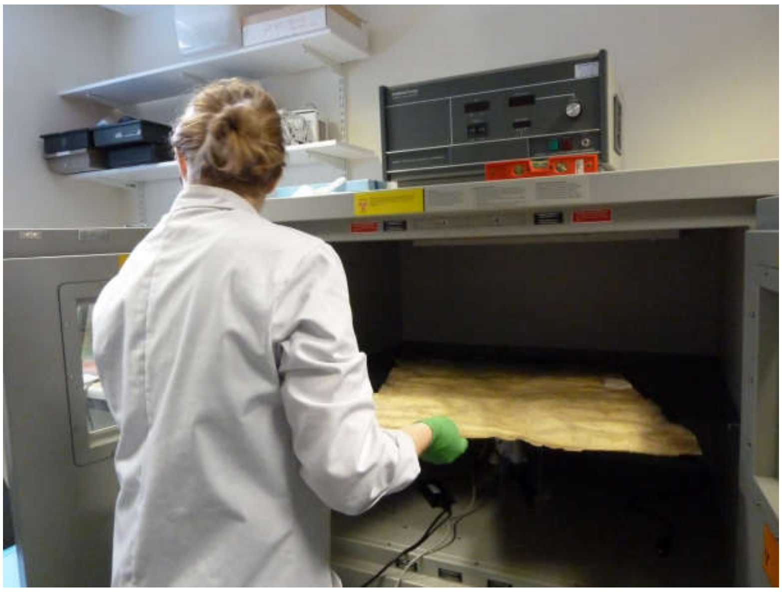
- The object should be secure but ideally mounted so that only air is on the other side.
- Object can be supported on a shelf with a window cutout for the pXRF measurements.
- A thick sheet of Teflon or some other low Z material can be placed as a barrier between object and mount.
- Mounts should be analyzed to determine contribution, if any, to the spectra.

Example of Object Support

- **pXRF is positioned below a shelf with a section cutout.**

Example of Object Support

- pXRF is positioned below a shelf with a section cutout.
- **The document is carefully placed onto shelf with area of interest positioned within the cutout area of the shelf.**



Example of Object Support

- pXRF is positioned below a shelf with a section cutout.
- The document is carefully placed onto shelf with area of interest positioned within the cutout area of the shelf.
- **The shelf cutout area allows for minimal repositioning of the pXRF analyzer without increased risk to the document.**

Issues Complicating Collection of Data

X-Ray Penetration Depth and Thin Samples

- Many documents are double-sided. PXRF will detect elements on both sides and sometimes on underlying material as well.
- Bound materials should be positioned so that the binding is not under strain.
- Inteleaving sheets of glassine, Teflon or other low Z materials between the page being analyzed and the underlying pages will reduce or eliminate contribution to the spectra.
- Best to analyze both sides of page to determine contribution to spectra.
- Blank areas on the documents should analyzed to determine contribution of the substrate.

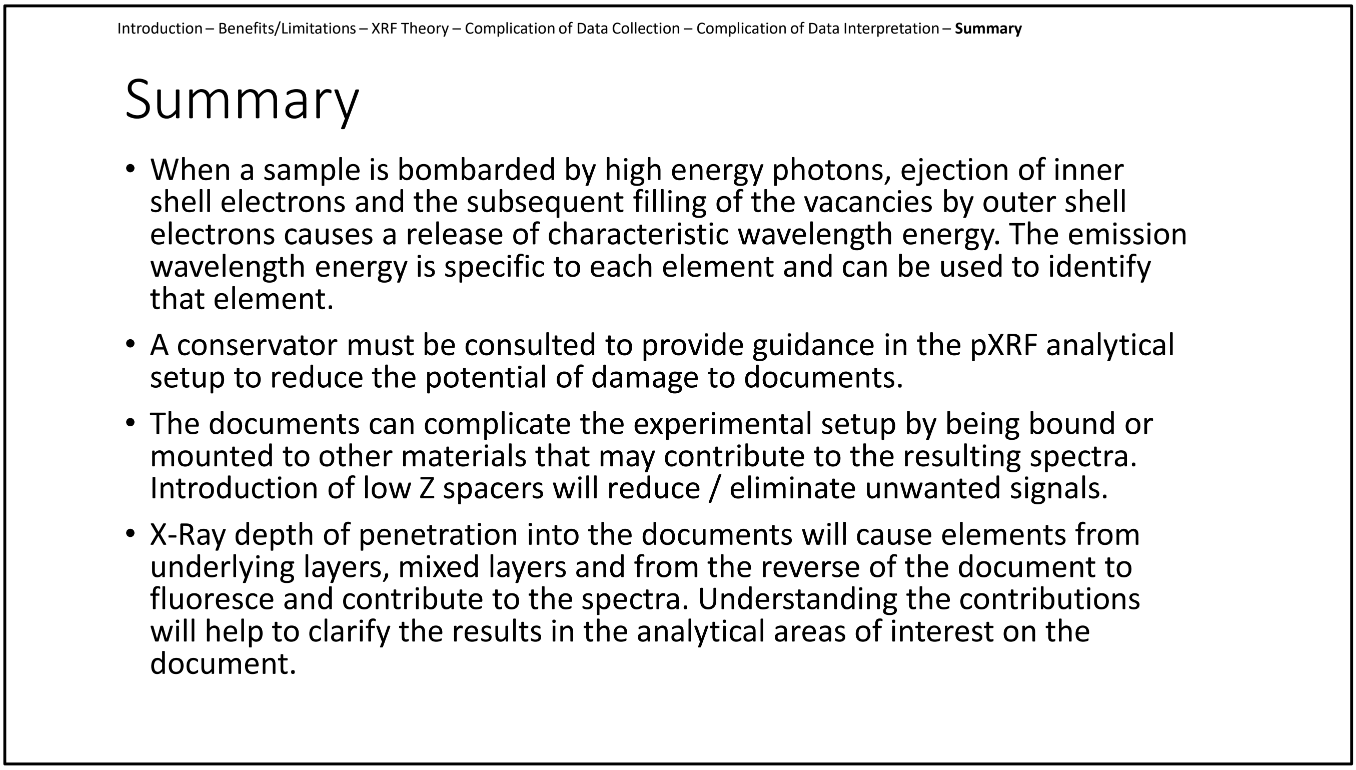
Book cradle

Introduction – Benefits/Limitations – XRF Theory – Complication of Data Collection – **Complication of Data Interpretation** – Summary

Issues Complicating Interpretation of Data

Interpretation Problems that are unavoidable

- Detected elements may be from both sides of document and even from the parchment or paper.
- Colourants may represent a mixture of colours.
- Illustrations or layers of colours may have been painted over.
- Elements detected may not be unique to a single colourant.
- Organic colourants (very low Z elements) will not be directly detected but can be inferred.
- Even with a collimator, the area of analysis may be too large for measurements of intricate details.



Summary

- When a sample is bombarded by high energy photons, ejection of inner shell electrons and the subsequent filling of the vacancies by outer shell electrons causes a release of characteristic wavelength energy. The emission wavelength energy is specific to each element and can be used to identify that element.
- A conservator must be consulted to provide guidance in the pXRF analytical setup to reduce the potential of damage to documents.
- The documents can complicate the experimental setup by being bound or mounted to other materials that may contribute to the resulting spectra. Introduction of low Z spacers will reduce / eliminate unwanted signals.
- X-Ray depth of penetration into the documents will cause elements from underlying layers, mixed layers and from the reverse of the document to fluoresce and contribute to the spectra. Understanding the contributions will help to clarify the results in the analytical areas of interest on the document.

Additional Notes:

Limit of Detection (LOD)	Level at which a characteristic peak can be confidently identified. Commonly used – Characteristic peak higher than 3 times the standard deviation of the background. Other factors can be used (see below).
Limit of Quantification (LOQ)	The level at which the element can be confidently quantified and that semi-quantitative ratio comparisons will be accurate. Commonly used – Characteristic peak is higher than 10 times the standard deviation of the background.

Additional Notes:

Standard Deviation (SD)	The quantified dispersion of a dataset. SD = $\sqrt{\frac{\Sigma(x-\mu)^2}{N}}$
Coefficient of Variance (C_V)	A measure of precision. Also known as relative standard deviation (RSD%). $C_V = \frac{SD}{\mu} * 100$ Precision can be increased by increasing live time acquisition. µ = average of multiple measurements.

Additional Notes:

Signal to Noise Ratio (SNR)

The standard process of determining SNR in many scientific analyses is conducted by dividing the peak intensity by the standard deviation (σ) of the background under the peak. The SNR of energy dispersive XRF is different due to sample geometry, density, thickness and consistency which directly affect the background. The relationship between the specimen and the background require a more vigorous method of calculating noise (N) that takes the sample matrix into account (Ernst et al. 2014). The accepted expression for N in this relationship is the square root of the background under the peak of interest.

$$N = \sqrt{Background\ Intensity}$$
$$SNR = Net\ Peak\ Intensity/N$$

Range of Result = 0 to infinity
Limit of Detection (SNR = 3)
Limit of Quantification (SNR = 10)

Reference: Ernst, T. and Berman, T. and Buscaglia, J. and Eckert-Lumsdon, T. and Hanlon, C. and Olsson, K. and Palenik, C. and Ryland, S. and Trejos, T. and Valadez, M. and Almirall, J. R. 2014. Signal-to-noise ratios in forensic glass analysis by micro X-ray fluorescence spectrometry. *X-Ray Spectrometry* 43(1), pp. 13-21.

Additional Notes:

Check out...

http://www.xrf.guru/
Great site covering many facets of pXRF analysis

https://groups.google.com/forum/#!forum/pxrf
PXRF for Cultural Heritage – Answers to questions

Recommended Texts

- Shugar, A. N. and Mass, J. L. eds. 2012. *Handheld XRF for Art and Archaeology*. Leuven: Leuven University Press.
- Jenkins, R. 1999. *X-Ray Fluorescence Spectrometry*. New York: John Wiley and Sons.
- Potts, P. J. and West, M. 2008. *Portable X-Ray Fluorescence Spectrometry*. Cambridge: RSC Publishing.